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RAMAN SPECTROSCOPIC STUDIES OF UREA INCLUSION COMPOUNDS CONTAINING α,ω-DIBROMOALKANE GUESTS

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Abstract Raman spectroscopic investigations of urea inclusion compounds containing α,ω-dibromoalkane [$Br(CH_2)_nBr$; n = 7-10] guest molecules are reported. Vibrational modes due to the urea confirm the structural identity of the inclusion compounds, and assignments of lattice modes due to the urea channel structure are also discussed. Investigations of the vibrational properties of the α,ω-dibromoalkane molecules included within this host structure have focused on the longitudinal acoustic mode and the C-Br stretching vibrations. The spectral bands due to the ν(C-Br) mode have been used to assess the relative amounts of trans and gauche end-groups in the included α,ω-dibromoalkane molecules.

Keywords: urea inclusion compounds, raman spectroscopy, conformational properties, vibrational properties, vibrational properties, α,ω-Dibromoalkane/urea inclusion compounds

1. INTRODUCTION

We are currently investigating several physico-chemical properties of the channel inclusion compounds that urea forms with appropriate organic "guest" molecules, and in this paper we report studies of urea inclusion compounds containing α,ω-dibromoalkane [$Br(CH_2)_nBr$] guests. The prin-

cipal aims underlying our work on these systems have been to further our understanding of the following properties of the guest molecules:
(i) periodic structural properties (investigated by single crystal X-ray diffraction); (ii) conformational properties (investigated by polarised Raman spectroscopy); and (iii) dynamic properties (investigated by incoherent quasielastic neutron scattering and NMR spectroscopy). The discussion here is restricted to the first two of these considerations: after briefly reviewing the structural properties deduced via X-ray diffraction, we focus upon the results of our Raman spectroscopic investigations.

2. GENERAL STRUCTURAL PROPERTIES

In urea inclusion compounds[1], the urea ($H_2N.CO.NH_2$) molecules pack in a channel-containing "host" structure (hexagonal, space group $P6_122$), within which "guest" molecules are located. The periodic repeat distances (denoted c_h and c_g respectively) of the host and guest molecules along the channel axis (c) are generally incommensurate; i.e. no small integers m and n can be found for which $m\,c_g = n\,c_h$. It is then convenient to consider the inclusion compound as being composed of distinguishable (but not independent) host and guest substructures. Each substructure can be represented by a basic structure (with three-dimensional periodicity) which is subjected to an "incommensurate modulation" (arising from host-guest interaction).

For the α,ω-dibromoalkane guests, X-ray diffraction has shown[2] that each single crystal contains regions in which the guest molecules are ordered only in one dimension (along c) and also regions in which the guest molecules are three-dimensionally ordered (i.e. both intrachannel and interchannel ordering). In the latter regions, the offset between the positions of the guest molecules in adjacent channels is $\Delta_g = c_g/3$ (Δ_g and c_g are defined in Figure 1), and the average basic guest structure in these regions is rhombohedral. Thus Δ_g increases with molecular length (i.e. as c_g increases), in contrast to the situation for urea inclusion compounds containing other families of guest molecules[3].

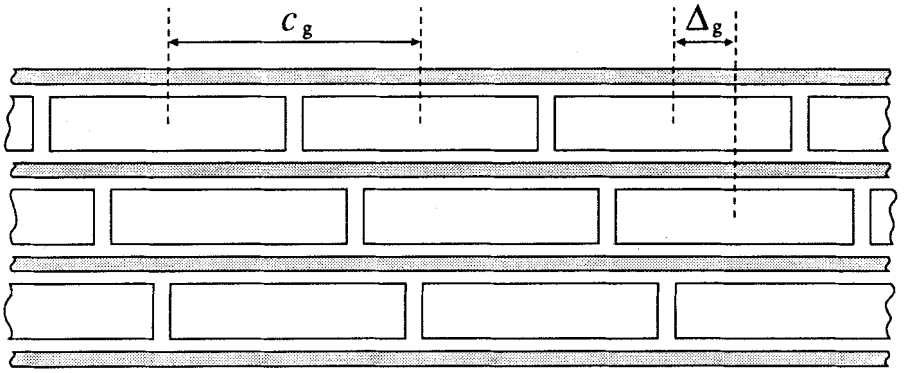

FIGURE 1 Definitions of c_g and Δ_g.

The n-alkane/urea inclusion compounds are known[4] to undergo a phase transition at a temperature that depends on the length of the guest molecule, and detailed X-ray diffraction studies[5] have shown that the basic host structure (which is hexagonal at room temperature) becomes orthorhombic in the low-temperature phase. Differential scanning calorimetric studies suggest that the α,ω-dibromoalkane/urea inclusion compounds also undergo a phase transition at low temperature, and it is probable that the basic host structure in the low-temperature phase for these compounds is also orthorhombic.

3. OBJECTIVES OF RAMAN SPECTROSCOPIC STUDIES

The general purpose of our Raman spectroscopic studies was to further our understanding of the structural and conformational properties of α,ω-dibromoalkane/urea inclusion compounds in different temperature regimes. Specific objectives were: (i) to verify the existence of the hexagonal urea host structure (as opposed to "pure" crystalline urea, which is tetragonal); (ii) to assign lattice modes due to the urea channel structure; and (iii) to investigate the vibrational properties of the α,ω-dibromoalkane guests, with particular regard to the longitudinal acoustic mode (LAM-1) and the ν(C-Br) stretching modes.

4. EXPERIMENTAL

Raman spectra of $Br(CH_2)_nBr$/urea single crystals were recorded as a function of: (i) molecular length (n = 7-10); (ii) experimental polarisation (ZZ, XZ, and XY); and (iii) temperature (-180°C and 25°C, denoted LT and HT respectively). In all experiments, the urea channel axis (crystallographic c axis (i.e. the long axis of the hexagonal prismatic morphology)) was aligned along the Z axis of the laboratory-fixed reference frame. No specific orientational relationship was established between the crystallographic a and b axes and the laboratory X and Y axes.

5. VIBRATIONAL MODES DUE TO UREA

The structural identity of our samples at HT has been verified by the presence of vibrational frequencies characteristic of the hexagonal urea host structure - in particular: (i) a very intense ν_s(CN) vibration (symmetry A_1) at 1025 cm^{-1}; and (ii) two δ(NCO) bending modes at 608 cm^{-1} (symmetry E_1) and 530 cm^{-1} (symmetry A_1). In contrast, tetragonal urea at HT is characterised[6] by the following modes: (i) ν_s(CN) at 1010 cm^{-1}; and (ii) δ(NCO) at 556 cm^{-1} and 570 cm^{-1}.

Bands arising from external vibrations (lattice modes) of urea occur at low frequency (<300 cm^{-1}), and two of these bands have been assigned to specific vibrational modes. One occurs at 185 cm^{-1} at LT and is polarised XY: its frequency decreases markedly on increasing temperature (to 164 cm^{-1} at HT). This mode corresponds to "breathing" of the urea channel in the plane perpendicular to the c axis; the large difference between the vibrational frequencies at LT and HT is probably associated with the marked change in the lattice parameters a_h and b_h at the phase transition[7]. The other lattice mode that has been assigned explicitly is at 132 cm^{-1} and is polarised ZZ; this mode corresponds to "breathing" of the urea channel in the c direction. The variation of vibrational frequency with temperature is much smaller for this mode than for the mode, discussed above, involving "breathing" in the plane perpendicular to the c axis.

6. VIBRATIONAL MODES DUE TO THE DIBROMOALKANE

6.1 The longitudinal acoustic mode (LAM)

LAM modes correspond to stationary vibrational waves with one or more nodes in the longitudinal displacements of the skeletal carbon atoms[8]. Only modes with an odd number of nodes are Raman active, and Raman intensity strongly decreases with increasing number of nodes. The LAM-1 mode (Figure 2) therefore gives rise to the strongest LAM band in the Raman spectrum. As either the end-group mass or the chain length is increased, the LAM-1 frequency decreases.

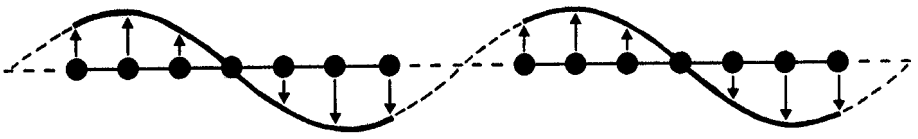

FIGURE 2 Schematic representation of the vibrational displacements for the LAM-1 mode (for clarity, the longitudinal displacements are represented here as transverse).

The existence of the LAM-1 mode (which is strongly ZZ polarised) confirms that there are α,ω-dibromoalkane guests in the trans conformation (linear, extended chains) within the urea channels. The LAM-1 frequencies for the α,ω-dibromoalkane/urea inclusion compounds are shown in Table 1. (Note that the HT values cannot be determined accurately since the LAM-1 band broadens considerably at high temperature.) Experimental values for the "pure" crystalline phases of the α,ω-dibromoalkanes at LT are also given for comparison. The LAM-1 band for 1,8-dibromooctane/urea at LT is shown in Figure 3.

Work is in progress to rationalise our experimental observations of the LAM-1 mode by extending the theoretical coupled-chain model of Minoni and Zerbi[8]. This model treats the guest molecule as an infinite one-dimensional system with a repeat unit comprising a single chain (molecule).

The real molecular geometry is approximated by a linear array of point masses, and the parameterisation within the model consists of the intrachain and interchain bond strengths and the values of the point masses. The results obtained by applying this model to rationalise the LAM-1 frequencies for the α,ω-dibromoalkane/urea inclusion compounds will be discussed in a future paper.

TABLE 1 LAM-1 frequencies.

	Vibrational frequency/cm^{-1}		
	pure $Br(CH_2)_nBr$	$Br(CH_2)_nBr$/urea	
	LT	LT	HT
n = 7	216	212	204
n = 8	150	151	149
n = 9	120	114	113
n = 10	126	110	hidden

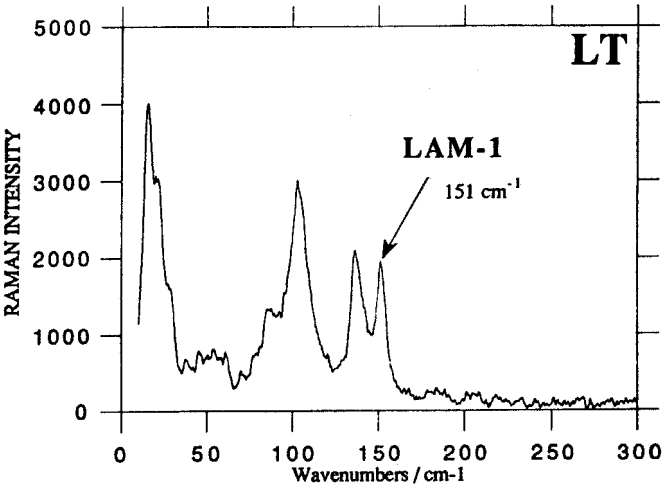

FIGURE 3 Raman spectrum (recorded in ZZ polarisation) illustrating the LAM-1 mode for 1,8-dibromooctane/urea at LT.

6.2 C-Br stretching mode

Although the central portions of the α,ω-dibromoalkane molecules in the urea channel are in the trans conformation, there may be a proportion of

end-groups in the gauche conformation. The extent of these "gauche defects" can be evaluated from the relative Raman intensities of the ν(C-Br) stretching bands for the trans and gauche end-group conformations, which occur at ~657 cm^{-1} and ~570 cm^{-1} respectively in the HT phase. Spectra illustrating the ν(C-Br) stretching bands for 1,10-dibromodecane/urea at LT and HT are shown in Figure 4. As expected, the band corresponding to the ν(C-Br) stretching mode for the trans end-group conformation is significantly more intense and is polarised ZZ; the ν(C-Br) stretching mode for the gauche end-group conformation is less strongly ZZ polarised. As a consequence, the ratio ($I_{ZZ}(gt)/I_{ZZ}(tt)$) of the Raman intensities, recorded in the ZZ polarisation, of the ν(C-Br) stretching bands for the gauche (gt) and trans (tt) end-group conformations represents a *lower limit* for the ratio (P(gt)/P(tt)) of the probabilities of occurrence of these end-group conformations.

Measured values of $I_{ZZ}(gt)/I_{ZZ}(tt)$ are given in Table 2. On the basis of these results, the percentage ($\mathcal{G}$) of gauche end-groups:

$$\mathcal{G} = \frac{100 \times P(gt)}{P(gt) + P(tt)}$$

for the α,ω-dibromoalkane guests is greater than ~7% for all chain lengths and both temperatures studied (with the exception of 1,9-dibromononane at LT, which is inexplicably anomalous). It is interesting to note from these results that the percentage of gauche end-groups does not vary significantly with temperature.

TABLE 2 Relative intensities (measured in ZZ polarisation) of the ν(C-Br) band for the gauche and trans end-group conformations.

	$I_{ZZ}(gt)/I_{ZZ}(tt)$	
n	LT	HT
7	0.135	0.168
8	0.090	0.071
9	0.028	0.120
10	0.085	0.091

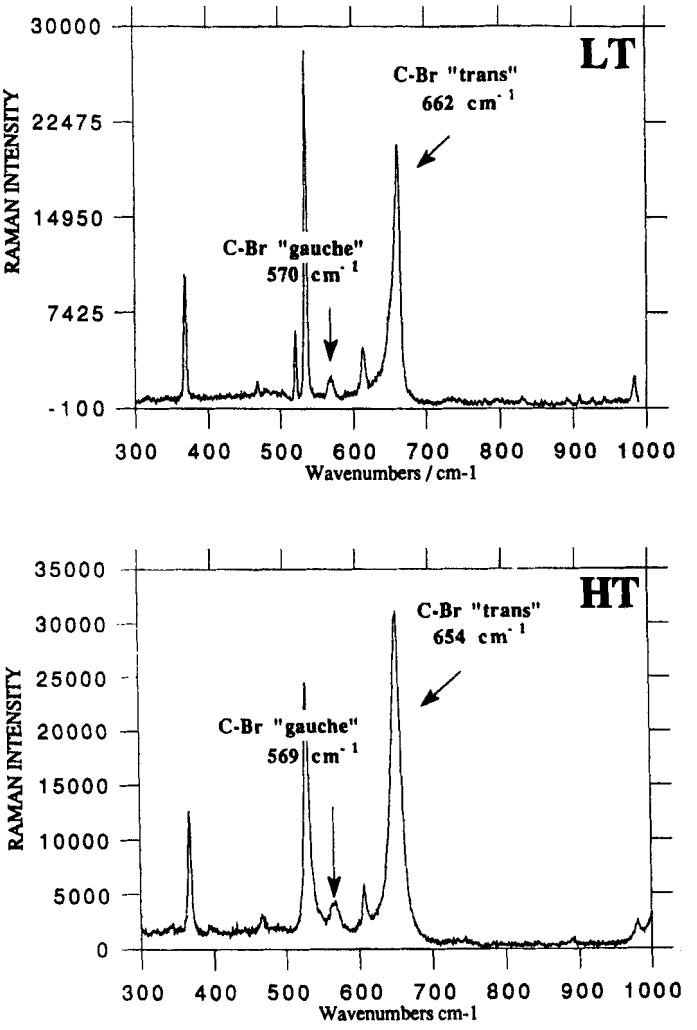

FIGURE 4 Raman spectra (recorded in ZZ polarisation) showing the ν(C-Br) stretching bands for the trans and gauche end-group conformations of 1,10-dibromodecane in its urea inclusion compound.

It is instructive to compare these values with those obtained for n-alkanes ($CH_3(CH_2)_nCH_3$) in urea. The percentage of gauche end-groups in n-alkane/urea inclusion compounds has become a source of much controversy and a wide range of values has been reported in the literature (Table 3).

TABLE 3 Literature values for percentage ($\mathcal{G}$) of gauche end-groups in $CH_3(CH_2)_nCH_3$/urea inclusion compounds (MDS = molecular dynamics simulation).

Reference	n	$\mathcal{G}$	Method
Kobayashi *et al*[9]	14-22	~ 5	Raman
Casal[10]	13-19	< 3	Infrared
Vold *et al*[11]	19	40	NMR and MDS
Imashiro *et al*[12]	7-10	16-25	NMR and MDS

In Raman spectra of n-alkanes included in urea, the frequency of the methyl group rocking mode is very similar for the trans and gauche end-group conformations, rendering a reliable assessment of $\mathcal{G}$ difficult. In contrast, Raman spectroscopy represents a more satisfactory approach for the α,ω-dibromoalkane guests, since assignment of the spectral bands due to the C-Br stretching modes of the different end-group conformations is considerably less ambiguous.

7. REFERENCES

1. K.D.M. Harris and J.M. Thomas, J. Chem. Soc., Faraday Trans., 86, 2985 (1990).
2. K.D.M. Harris, S.P. Smart and M.D. Hollingsworth, J. Chem. Soc., Faraday Trans., in press.
3. K.D.M. Harris and M.D. Hollingsworth, Proc. Roy. Soc. A, 431, 245 (1990).

4. R.C. Pemberton and N.G. Parsonage, Trans. Faraday Soc., 61, 2112 (1965).
5. Y. Chatani, Y. Taki and H. Tadokoro, Acta Crystallogr., Sect. B, 33, 309 (1977).
6. V. Fawcett and D.A. Long, J. Raman Spectrosc., 3, 263 (1975).
7. Y. Chatani, H. Anraku and Y. Taki, Mol. Cryst. Liq. Cryst., 48, 219 (1978).
8. G. Minoni and G. Zerbi, J. Phys. Chem., 86, 4791 (1982).
9. M. Kobayashi, H. Koizumi and Y. Cho, J. Chem. Phys., 93, 4659 (1990).
10. H.L. Casal, J. Phys. Chem., 94, 2232 (1990).
11. R.L. Vold, R.R. Vold and N.J. Heaton, Adv. Magn. Reson., 13, 17 (1989).
12. F. Imashiro, D. Kuwahara, T. Nakai and T. Terao, J. Chem. Phys., 90, 3356 (1989).